

(c)

〔10〕中华人民共和国专利局

〔11〕审定号 CN 1003353B



## 〔12〕发明专利申请审定说明书

〔21〕申请号 85100111

〔51〕Int.Cl.  
B01J 8/06

〔44〕审定公告日 1989年2月22日

〔22〕申请日 85.4.1

〔71〕申请人 清华大学

地 址 北京市海淀区清华园

〔72〕发明人 金 涌 姚文虎

〔74〕专利代理机构 清华大学专利事务所

代理人 王 兵

B01J 19/24 F28D 13/00

说明书页数： 4 附图页数： 2

〔54〕发明名称 在列管式固定床反应器中进行催化反应的方法及装置

## 〔57〕摘要

一种在列管式固定床反应器中进行催化反应的方法及装置，属于高溫列管式固定床反应器中新换热方式领域。本发明的特征在于固定床反应器列管间进行气固流化换热的固体颗粒为球形硅胶，金属铝粉或砂粒，颗粒平均直径为80~120μ，颗粒球形度>0.95，且气体分布器压降为床层压降的0.5~0.8倍。本发明提供的装置的特征在于气体分布器具有最佳开孔率、孔间距和列管间距。本发明可延长催化剂寿命，节约投资，提高产品收率，转化率和质量。

V2

85 1 00111

1

2

### 权利要求书

1. 一种在列管式固定床反应器中进行催化反应的方法，列管内装有催化剂，列管间采用气固流化床换热，由流化气或部分循环的颗粒带走热量以控制反应温度，其特征在于列管间的固体颗粒为球形硅胶，颗粒平均直径为 $80\sim120\mu$ ，颗粒球形度 $>0.95$ ，且气体分布器压降为床层压降的0.5~0.8倍。

2. 按照权利要求1所说的在列管式固定床反应器中进行催化反应的方法，其特征在于所说的列管间固体颗粒为金属铝粉。

3. 按照权利要求1所说的在列管式固定床反应器中进行催化反应的方法，其特征在于所说的列管间固体颗粒为砂粒。

4. 采用流化床换热的列管式固定床反应器，其中管间装有固体颗粒，下部为多管式气体分布器(8)，分布器(8)向下开的出气孔(14)为短管，其特征在于，气体分布器的开孔率为0.5~0.8%，孔间距为80~120mm，列管间距为：

$$t_1 = (1.5 \sim 2.5)d, t_2 = (1.25 \sim 1.75)d, \text{ 式中 } d \text{ 为列管管径。}$$

5. 按照权利要求4所说的反应器，其特征在于所说的气体分布器有套管式支管，它由外套管(18)、内套管(19)和接口(20)组成，内套管(19)上有向上的开孔(17)，外套管(18)上有向下的开孔(15)。

本发明涉及高温列管式固定床反应器中新的换热方式。

热效应较大的催化反应一般在列管式反应器中进行，有效的换热方式可使释放的大量反应热及时移出催化床层，避免发生催化剂烧结事故。

国内外一般采用熔盐作为高温下的列管式固定床反应器的换热介质（基本有机化学工程，天津大学编，1978，人民教育出版社）。通过熔盐在列管束间的强制流动达到移热目的。熔盐流动性差，传热系数小，往往造成反应器内较大的轴径向温差。熔盐在高温下具有强腐蚀性，因腐蚀造成泄漏时，将导致恶性爆炸事故。熔盐泵价值昂贵，采用熔盐体系换热时，需要较高的投资费用。

后来金涌等人提出了一种在列管式固定床反

应器中进行液化换热的方法及装置（见“采用流化床换热的固定床反应器”，化学工程1979年第1期，金涌等人）。该方法是在列管式固定床反应器的管内装有催化剂并进行催化反应，在管侧采用气固流化床进行换热，由流化气及部分循环的固体颗粒带走热量以控制反应器温度。该方法的具体结构由附图1、2、3给出。图1为反应器及附属设备的工艺流程，图2为多管式气体分布器在反应器内的布置形式，图3为多管式气体分布器的结构形式。图1中(2)为列管式固定床反应器的主体部分，在列管(10)内充填催化剂，用来催化化学反应、反应气体（原料气）经反应器顶部文丘里形的进口气体分布器(6)由上至下流经列管，进行催化反应，最后从出口(12)引出反应器，在管束间充填固体颗粒，用于流化换热，其用量由工艺计算确定。反应器中列管束以花板(9)固定，流化所用气体（如空气）经流化气体分布器(8)由下至上进入管束间进行换热，然后经废热锅炉(11)回收热量，再经旋风分离器(4)回收夹带的固体颗粒后放空，所回收的固体颗粒可储存于中间储槽(5)，或再经加料装置(7)加入反应器。本发明可根据工艺要求设计为不循环式或部分循环式。为此，在反应器下部侧面设有固体颗粒循环用储槽(3)，循环颗粒由反应器流出后，用空气提升，经旋风分离器(4)收尘后存于中间储槽(5)，再经加料装置(7)后进入反应器，完成部分循环。循环用储槽(3)亦可供停车时卸出换热固体介质使用。

流化气体分布器(8)是该装置的主要部件，承担着均匀布气，提供良好的初始流化条件的任务，为满足正常流化操作要求，必须合理选择和设计流化气体分布器。考虑到列管式固定床反应器内具有大量列管的特点，所以采用了多管式气体分布器。图2中列出多管式气体分布器在反应器内与列管的布置形式，流化气体由反应器两侧进入集气管(13)再分别进入气体分布器支管(16)，向下喷出。气体分布器支管部分的结构如图3所示，其特征在于气体出气口设在支管的下方，将气体向上喷入流化床层，在穿透一定床层厚度后，返回改为向下鼓泡穿过颗粒床层，为了防止停车时颗粒进人气体分布管道造成堵塞，气体分布器的支管出气口为短管(14)。

2

85 1 00111

3

上述在列管式固定床反应器中进行流化换热的方法和装置，既保留了固定床反应器转化率和收率较高的优点，又避免了熔盐换热的缺点。但由于该方法没有对气体分布器的设计数据做出具体的规定，因而还不能很好地实施。

本发明的目的是要进一步完善上述方法和装置，进一步发挥其优点并使其能在工业实践中很好地实施。

本发明为一种在列管式固定床反应器中进行催化反应的方法，其中列管内部装有催化剂，列管间采用气固流化床换热，由流化气或部分循环的颗粒带走热量以控制反应温度，其特征在于列管间的固体颗粒为球形硅胶，金属铝粉或砂粒，颗粒平均直径为 $80\sim120\mu$ ，颗粒球形度 $>0.95$ ，且气体分布器压降为床层压降的 $0.5\sim0.8$ 倍。

采用上述种类和规格的固体颗粒，可以保证良好的流化质量，提高流化换热的效率。为确保布气均匀，气体分布器必须具有一定压降，选用合适的分布气压降，是分布器设计的又一环。上述气体分布器压降的选用，依据如下：

$$\Delta P_{\text{分布器}} = (0.5\sim0.8)H_{\text{op}}$$

式中， $H_{\text{op}}$ 为床层压降

$H_{\text{o}}$ —流化床静床高

$P_{\text{r}}$ —堆比重

为实施在列管式固定床反应器中进行催化反应的方法，本发明设计出一种采用流化床换热的列管式固定床反应器，其中列管间装有固体颗粒，下部为多管式气体分布器（8），气体分布器的支管出气口为短管（14），其特征在于气体分布器的开孔率 $0.5\sim0.8\%$ ，孔间距为 $80\sim120\text{mm}$ ，列管间距（见附图2）为：

$$t_1 = (1.5\sim2.5)d, \quad t_2 = (1.25\sim1.75)d, \quad \text{式中 } d \text{ 为列管直径。}$$

气体分布器的正确设计是实施本发明的核心，按照本发明提供的气体分布器，可以获得好的流化换热效果。

本发明还对气体分布器的支管进行了改进，采用一种套管式支管。现结合附图4进行详细的说明，附图4为套管式气体分布器支管，图中（16）为气体分布器支管，它由外套管（18），内套管（19），接头（20）组成，内套管（19）上有向上的开孔（17），外套管（18）有向下的开孔

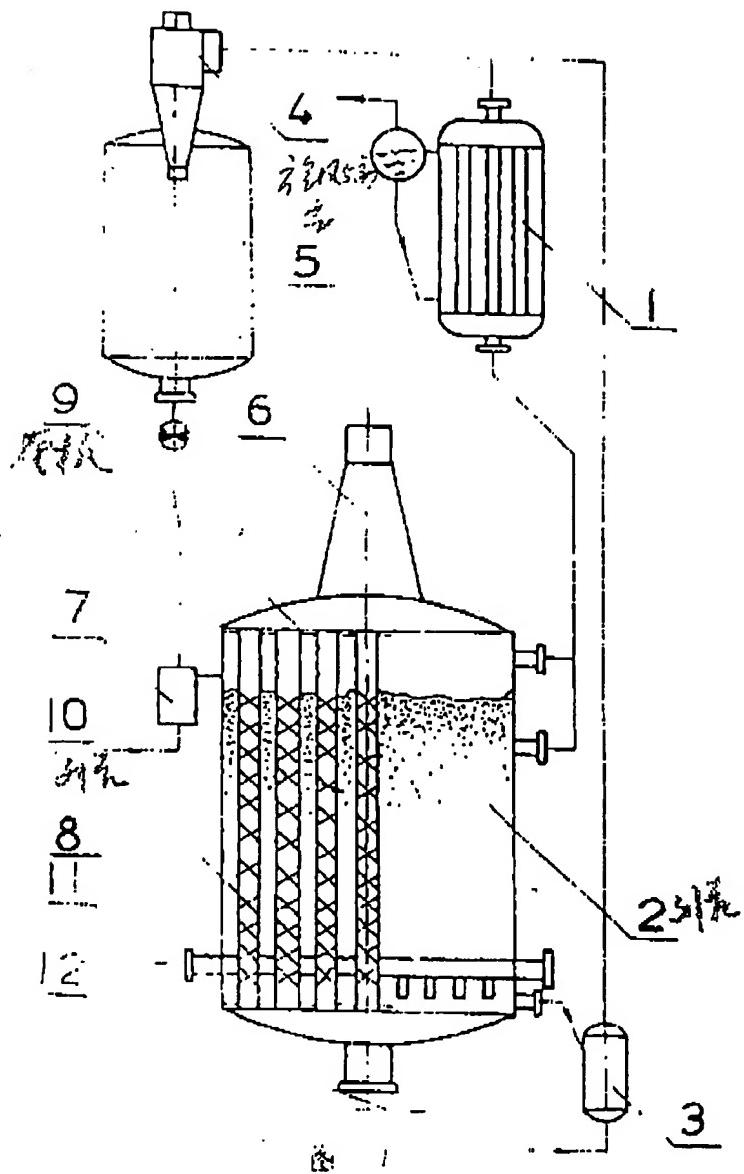
4

（15）。气体由接口（20）进入内套管（19），由开孔（17）流出，再从外套管（18）的开孔（15）中向下流入流化床层。该种结构可以达到与短管（14）同样的效果。现例举实施例如下：

在生产异烟肼工艺中，生产4-氨基吡啶的反应过程，采用直径为16米的列管式固定床反应器，内装637根外径为32毫米、内径为25毫米的列管，管内充填 $d_p=3$ 毫米球形硅胶颗粒，所用分布器为多管式下吹型，开孔率0.6%，孔间距100毫米，列管间距 $t_1=70$ 毫米， $t_2=45$ 毫米为保证布气均匀，选用分布气压降为1500毫米水柱。反应器在 $360^{\circ}\text{C}$ 下操作，换热介质的流化线速度为0.3米/秒。该反应器可以达到年产2000吨4-氨基吡啶的生产能力。

采用本发明的上述反应器，保持了固定床反应器原有的优点，可以达到较高的转化率和收率，换热方式则以流化床换热取代常用的熔盐换热，节约大量投资，操作简便。由于具有较高的传热系数，反应器内温度均匀，轴径向温差小于 $5^{\circ}\text{C}$ ，防止催化剂因受热不均，局部过热造成烧结，从而延长了催化剂的使用寿命。在具有副产品的催化反应中，反应器内温度均匀，有利于抑制副反应产生，使产品收率、转化率、产品质量得到提高。

申请号 85100111  
Int Cl. B01J 8/06  
审定公告日 1989年2月22日



申请号 85 1 00111  
 Int. Cl. B01J 8/06  
 审定公告日 1989年2月22日

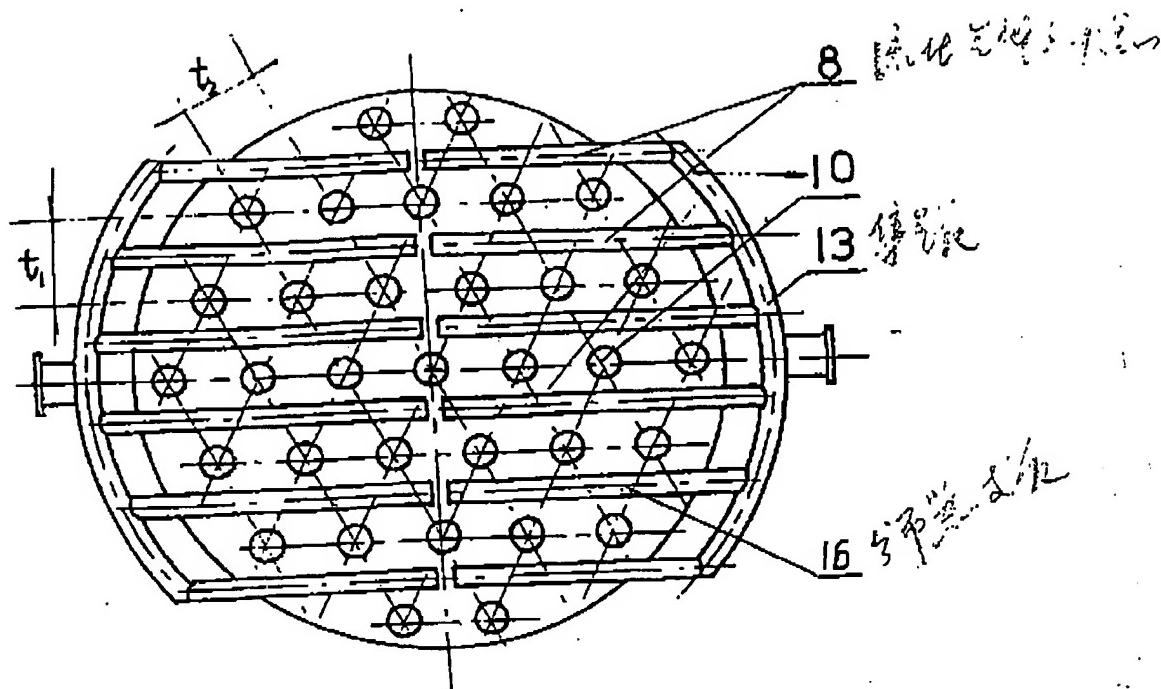


图 2

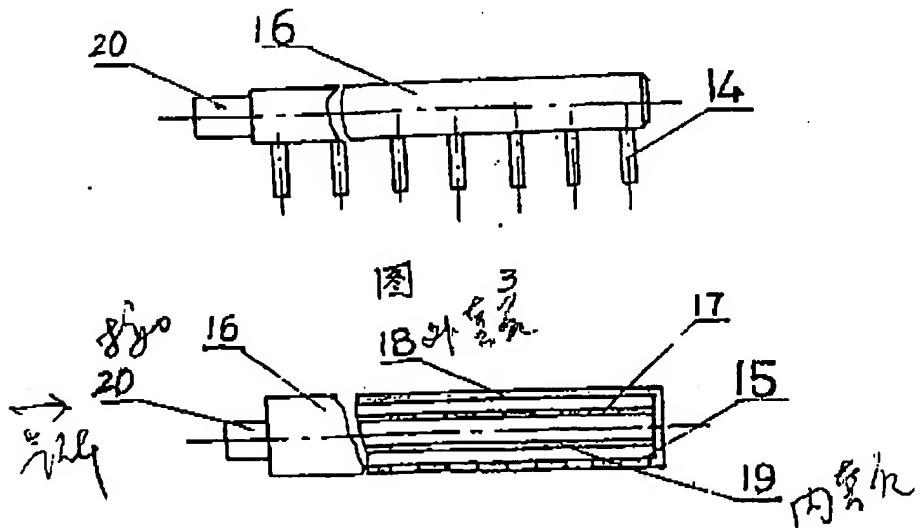


图 4

(c)

METHOD AND DEVICE FOR CONDUCTING CATALYTIC REACTION IN SHELL-AND-TUBE FIXED BED REACTOR

CN 1003353 B

The present invention relates to a new heat exchange mode in a high-temperature shell-and-tube fixed bed reactor.

The catalytic reaction having relatively greater heat effect is generally carried out in a shell-and-tube reactor, wherein the effective heat exchange mode enables a large amount of reaction heat to shift out of the catalyst bed layer in time, so that avoiding the accident of catalyst agglomeration.

At home and abroad, molten salt is generally used as a heat exchange medium in shell-and-tube reactor at high temperature (see, Basic Organic Chemical Engineering, Tianjin University, 1978, People's Education Press), the object of shifting heat is achieved through forced flow of molten salt among tubular bundle. However, molten salt is difficult to flow and has a low heat supply coefficient, thus, a relatively greater temperature difference both in axial and radial is resulted sometimes. Moreover, molten salt is highly corrosive at high temperature; If the corrosion results in leakage, a malignant explosion accident will occur. Further, a pump of molten salt is expensive, thus it needs a relatively higher investment cost when a molten salt system is used for heat exchange.

Afterward, Jing, Yong, et al put forward a method and a device for conducting fluidizing heat exchange in a shell-and-tube fixed bed reactor (see, Jin, Yong, et al, "A Fixed Bed Reactor with Fluidized Bed Type Heat Exchange", Chemical Engineering, 1979, No. 1). The method comprises carrying out catalytic reaction in a shell-and-tube reactor, wherein catalyst is packed in each reaction tube; subject tubes to heat exchange by using a gas-solid fluidized bed; and removing heat via fluidized gas and partially circulated solid particulate, whereby controlling the reactor's temperature. The specific frame of the method is given in Fig. 1, 2 and 3; Fig. 1: a process scheme of the reactor and its auxillary facilities; Fig. 2: arrangement form of multi-tube type gas distributor inside the reactor; and Fig. 3: structural form of multi-tube type

gas distributor. In Fig. 1, [2] is the main body of the shell-and-tube fixed bed reactor; tube [10] is packed with catalyst, which is useful for catalyzing chemical reaction. The reactive gas (feed gas) enters from a Venturi-type inlet gas distributor [6] on the top of the reactor and flows from top to bottom along the tubes to carry out catalytic reaction, and finally flows out of the outlet [12]. Solid particulate is packed among the tubes for fluidizing heat exchange, which amount is determined according to the practical process situation. The tubes in the reactor are fixed with figured pattern card [9]; the fluidizing gas (e.g., air) passes through a fluidizing gas distributor [8], enters the space among the tubes from top to bottom to conduct heat exchange, then its heat is recovered by a waste heat boiler [1], and solid particulate carried thereby is recovered by a cyclone separator [4] before the gas is discharged; the recovered solid particulate can be stored in a middle storage tank [5], or added to the reactor via a feed device [7]. The present invention is designed as non-circulating type or partially circulating type according to the process requirement. Therefor, a storage tank [3] for circulating solid particulate is installed at lower side of the reactor; the circulating particulate flows out of the reactor, is air hoisted, and stored in the middle storage tank [5] after being dedusted by the cyclone separator [4], and then enters the reactor via the feed device [7], so that accomplishing partial circulation. The circulating storage tank [3] also serves for the purpose of discharging the solid heat exchange medium when the reactor is shut down.

The fluidizing gas distributor [8] is a main element of the device; bearing the tasks of uniformly distributing gas and providing good initial fluidizing conditions, and shall be rationally selected and designed for meeting the requirement of normal fluidizing operation. In view of the feature of the shell-and-tube fixed bed reactor having a great number of tubes, a multi-tube gas distributor is used. Fig. 2 is the arrangement form of the multi-tube gas distributor and the tubes in the reactor; the fluidizing gas firstly enters a gathering tube [13] via two sides of the reactor and then respectively branches [16] of the gas distributor, and ejects downward. The part of branches of the gas distributor has a structure as shown in Fig. 3, which is characterized in that the gas outlets are at underside of the branches; the gas is firstly ejected

upward to the fluidizing bed layer, penetrates the bed layer till a certain thickness, and then returns downward to bubble through a particulate bed layer. For avoiding the entrance of particulate to the tubes of the gas distributor to cause clog when the reactor is shut down, the outlets of the branches of the gas distributor are spools [14].

The above method and device for conducting fluidizing heat exchange in a shell-and-tube fixed bed reactor not only retain the advantages of relatively higher conversion and yield possessed by a fixed bed reactor, but also avoid the shortcoming of heat exchange with molten salt. However, since the method makes no specific requirement on the data for designing the gas distribution, it is yet to be further perfected.

The object of the present invention is to further perfect the above method and device, for further exploiting the advantages thereof and better applying them in industrial practice.

The present invention relates to a method for conducting catalytic reaction in a shell-and-tube fixed bed reactor, wherein each tube of the reactor is packed with catalyst; heat exchange among the tubes is conducted via a gas-solid fluidizing bed; and heat is removed by a fluidizing gas or partially circulated particulate so that the reaction temperature is controlled; which is characterized in that the solid particulate among the tubes is spherical silica gel, metal aluminum powder or grit, having an average diameter of 80-120  $\mu$  and a sphericity of > 0.95; and the gas distributor has a pressure drop of 0.5-0.8 times based on that of the bed layer.

By using the solid particulate meeting above requirements, an excellent fluidizing quality can be assuredly obtained, and the efficiency of fluidizing heat exchange can be increased. To insure the gas distribution uniform, the gas distributor shall have a certain pressure drop; that is, the selection of a suitable gas distribution pressure drop is crucial for designing the distributor. The pressure drop for the gas distributor is calculated as follows:

$$\Delta P_{\text{distributor}} = (0.5-0.8)H_{\text{stack}}$$

wherein,  $H_{\text{stack}}$  is pressure drop of the bed layer;

$H_0$  is static height of the fluidizing bed;

$\rho_{\text{stack}}$  is stack specific weight.

In order to accomplish the method for conducting catalytic reaction in a shell-and-tube fixed bed reactor, the present invention designs a shell-and-tube fixed bed reactor with fluidized bed type heat exchange, wherein solid particulate is packed among the tubes, a multi-tube type gas distributor [8] is fixed at the lower part, and the outlets of the branches of the gas distributor are spools [14]; which is characterized in that the percentage of open area of the gas distributor is 0.5-0.8%, the pore interval is 80-120 mm, and the tube interval (see Fig. 2) is as follows:

$$t_1 = (1.5-2.5)d, t_2 = (1.25-1.75)d, \text{ wherein } d \text{ is diameter of the tube.}$$

The design of the gas distributor is crucial point of the present invention, and a good fluidizing heat exchange effect will be obtained by using the gas distributor provided in the present invention.

The present invention also relates to an improvement on the branches of the gas distributor, i.e., a kind of double-pipe branches is used. The double-pipe branches of the gas distributor are shown in Fig. 4, wherein [16] is gas distributor branch, which consists of outer sleeve [18], inner sleeve [19], and joint [20]. The inner sleeve [19] has upward opening [17] thereon, and the outer sleeve [18] has downward opening [15] thereon. The gas enters the inner sleeve [19] via the joint [20], flows out from the opening [17], and then downward to the fluidizing bed layer via the opening [15] of the outer sleeve [18]. This kind of structure brings about same effect as spools [14].

#### Example

In the process of producing isonicotinyl hydrazide, 4-cyanopyridine is prepared in a shell-and-tube fixed bed reactor of  $\phi 16$  m, wherein 637 tubes having an

outer diameter of 32 mm and an inner diameter of 25 mm are installed, each of the tubes is packed with spherical silica gel particles of  $d_p = 3$  mm; the distributor is multi-tube type down-blow one, which has a percentage of open area of 0.6%, a pore interval of 100 mm, and a tube interval of  $t_1 = 70$  mm and  $t_2 = 45$  mm, whereby the gas distribution is assured uniform; the gas distribution pressure drop is 1,500 mm ( $H_2O$ ); the reactor is operated at 360°C; and the fluidizing linear velocity of the heat exchange medium is 0.3 m/s. In this case, the production capacity of 4-cyanopyridine is up to 2,000 t/a.

The reactor of the present invention not only retains the original advantages of fixed bed reactor, i.e., relatively higher conversion and yield, but also saves a large amount of investment and is featured with simple operation by using a heat exchange mode of a fluidizing bed instead of the commonly used molten salt. Due to the relatively higher heat transfer coefficient, the temperature inside the reactor is uniform, the temperature difference both in axial and radial is less than 5°C, whereby avoiding the agglomeration of catalyst due to non-uniform heating and topical superheating, so that the use life of catalyst is extended. As for a catalytic reaction that generates side-products, the uniform temperature in the reactor is beneficial for inhibiting the occurrence of side-reaction, so that the product yield, the conversion and the product quality are increased.

## CLAIMS

1. A method for conducting catalytic reaction in a shell-and-tube fixed bed reactor, wherein each tube of the reactor is packed with catalyst; heat exchange among the tubes is conducted via a gas-solid fluidizing bed; and heat is removed by a fluidizing gas or partially circulated particulate so that the reaction temperature is controlled; which is characterized in that the solid particulate among the tubes is spherical silica gel having an average diameter of 80-120  $\mu$  and a sphericity of > 0.95; and the gas distributor has a pressure drop of 0.5-0.8 time based on that of the bed layer.
2. A method for conducting catalytic reaction in a shell-and-tube fixed bed reactor according to claim 1, which is characterized in that the solid particulate among the tubes is metal aluminum powder.
3. A method for conducting catalytic reaction in a shell-and-tube fixed bed reactor according to claim 1, which is characterized in that the solid particulate among the tubes is grit.
4. A shell-and-tube fixed bed reactor with fluidized bed type heat exchange, wherein solid particulate is packed among the tubes, a multi-tube type gas distributor [8] is fixed at the lower part, and the outlets opening downward of the gas distributor are spools [14]; which is characterized in that the percentage of open area of the gas distributor is 0.5-0.8%, the pore interval is 80-120 mm, and the tube interval is as follows:  
 $t_1 = (1.5-2.5)d$ ,  $t_2 = (1.25-1.75)d$ , wherein d is diameter of the tube.
5. A reactor according to claim 4, which is characterized in that the gas distributor has double-pipe branch, that consists of outer sleeve [18], inner sleeve [19], and joint [20]; the inner sleeve [19] has upward opening [17] thereon, and the outer sleeve [18] has downward opening [15] thereon.

**ABSTRACT**

A method and a device for conducting catalytic reaction in a shell-and-tube fixed bed reactor, which relates to a new heat exchange mode of a high temperature shell-and-tube fixed bed reactor. In the method of the present invention, the solid particulate that conducts gas-solid fluidizing heat exchange among the tubes of the fixed bed reactor is spherical silica gel, metal aluminum powder or grit, which has an average diameter of 80-120  $\mu$  and a sphericity of > 0.95; and the gas distributor has a pressure drop of 0.5-0.8 time based on that of the bed layer. In the device of the present invention, the gas distributor has the optimum percentage of open area, pore interval and tube interval. The use life of the catalyst is extended, the investment is saved, and the product yield, conversion and quality are increased.